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Published in:
Journal of Physical Chemistry C

DOI:
[10.1021/jp0751662](https://doi.org/10.1021/jp0751662)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2007

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Mendoza, S. M., Lubomska, M., Walko, M., Feringa, B. L., & Rudolf, P. (2007). Characterization by X-ray photoemission spectroscopy of the open and closed forms of a dithienylethene switch in thin films. *Journal of Physical Chemistry C*, 111(44), 16533-16537. <https://doi.org/10.1021/jp0751662>

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Characterization by X-ray photoemission spectroscopy of the open and closed forms of a dithienylethene switch in thin films.

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SUPPORTING INFORMATION

Materials and methods

Synthesis of the 1,2-dithienylethene (1,2-bis(5'-(pyridine-4''-yl)-2'-methylthien-3'-yl)cyclopentene).
n-BuLi (3 ml of 1.6 M solution in hexane, 4.8 mM) was added to the solution of 1,2-bis(5'-chloro-2'-methylthien-3'-yl)cyclopentene¹ (700 mg, 2.1 mM) in anhydrous THF (20 ml) kept under nitrogen atmosphere. This solution was stirred at room temperature for 30 min and then B(n-OBu)₃ (1.4 ml, 5.2 mM) was added. After another 1 h of stirring at room temperature 4-bromopyridine.HCl (875 mg, 4.5 mM), Pd(PPh₃)₄ (49 mg, 0.042 mM) and aqueous Na₂CO₃ (10 ml of 2M solution) were added. The

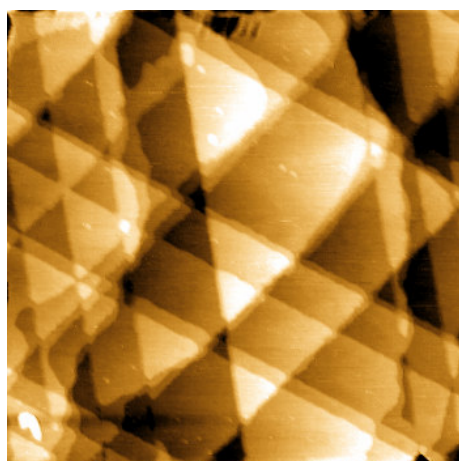
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resulting two-phase mixture was heated to reflux for 3 h and then allowed to cool to room temperature. Diethyl ether (50 ml) and water (50 ml) were added and organic layer was separated and dried over Na_2SO_4 . After evaporation of the solvent, the product was purified by column chromatography (SiO_2 , methanol/ $\text{CH}_2\text{Cl}_2 = 1/20$) to give a white solid (580 mg 67%).

^1H NMR (CDCl_3 , 300 MHz) δ_{H} 2.04 (s, 6H), 2.06-2.16 (m, 2H), 2.87 (t, $J=7.2$ Hz, 4H), 7.22 (s, 2H), 7.36 (d, $J=5.7$ Hz, 4H), 8.53 (d, $J=5.1$ Hz, 4H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ_{C} 14.5 (q), 22.87 (t), 38.2 (t), 119.1 (d), 126.2 (d), 134.6 (s), 136.4 (s), 136.9 (s), 137.2 (s), 141.2 (s), 149.8 (d); HRMS calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{S}_2$ 414.122, found 414.121.

Preparation of gold on mica. Au(111) substrates were prepared by vacuum sublimation (10^{-7} Torr) of gold (99,99% Umicore Materials AG,) onto freshly cleaved mica sheets preheated at 375 °C in a custom-built evaporator. Prior to use, each substrate was annealed with a hydrogen flame to improve the surface reconstruction and remove possible environmental contamination. The result of this procedure was gold substrates (111) oriented. Figure A shows STM images of the crystalline substrate characterized by terraces with triangular shape – due to the (111) orientation – (top) and herringbone structures arising from the ($\sqrt{3} \times 23$) surface reconstruction (bottom).^{2,3}



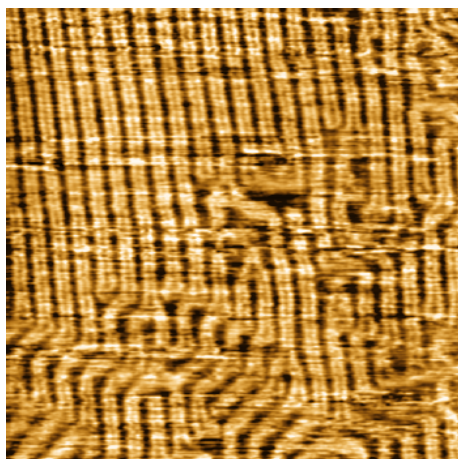


Figure A. STM images of a freshly prepared gold on mica substrate. Top: $472 \times 472 \text{ nm}^2$ area scanned in air at 0.2 nA tunneling current and -200 mV bias voltage. The gold substrate have terraces with triangular shape, as expected for Au(111). Bottom: $140 \times 140 \text{ nm}^2$ area scanned in tetradecane at 20 pA tunneling current and 700 mV bias voltage. The picture shows the herringbone structure, characteristic of the Au(111) surface reconstruction.

Stability of the dithienylethene switch under X-ray irradiation in ultra high vacuum.

It is very well known that X-ray irradiation can induce damage in organic compounds.^{4, 5} To test the stability of the dithienylethene switch under irradiation, we exposed the thin film to the X-rays and followed the evolution of the photoemission signals while irradiating. Figure B presents the evolution of S 2*p* core level obtained after 10, 40 and 70 minutes of continuous X-ray irradiation of the closed form of the switch. Initially, the photoemission peak shows only one component with maximum intensity at 163.4 eV as mentioned in section 1 of the article. The photoemission signal remains unchanged after 40 minutes of the irradiation. After 70 minutes of X-ray irradiation a new component appeared at 164.5 eV binding energy, accompanied by broadening of the C 1*s* core level (not shown here), that indicates the decomposition of the dithienylethene switch. Since the observed changes do not correspond to the appearance of S 2*p* and C 1*s* components typical of a closed form (compare with Figs. 2 and 4 in the article), we can exclude switching induced by X-rays.

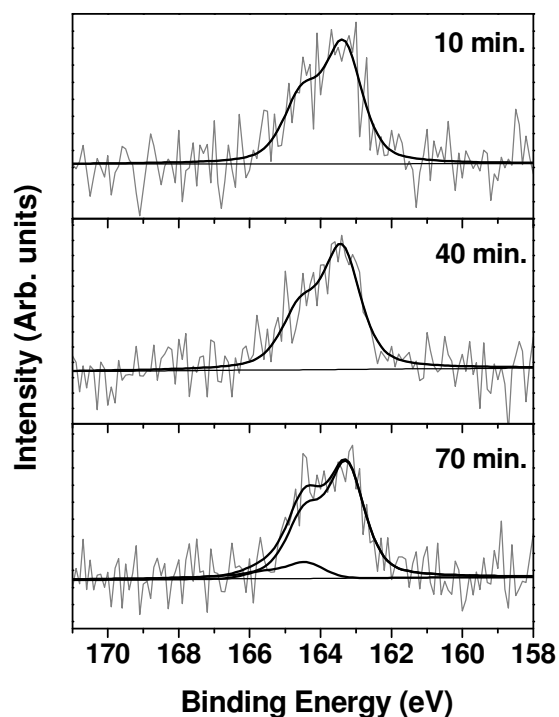


Figure B. Evolution of the S 2*p* core level photoemission signal collected after 10, 40 and 70 minutes of X-ray irradiation of the closed dithienylethene switch multilayer film on Au(111). Experimental data (—) and fit (—) .

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